

Rec'd PCT/PTO 22 MAR 2005



101528629



PCT/GB 2003 / 004181



INVESTOR IN PEOPLE

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

REC'D 23 JAN 2004

WIPO PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

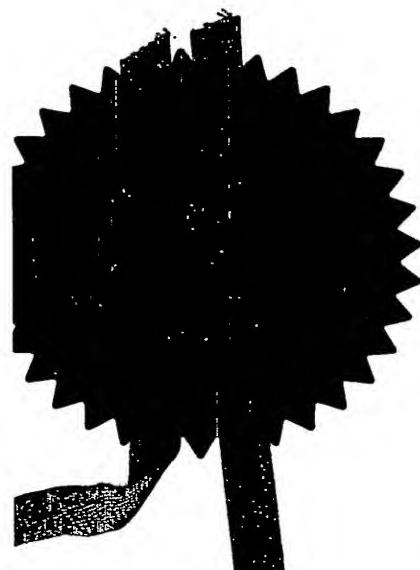
In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

BEST AVAILABLE COPY

Signed

Dated 10 November 2003





27SEP02 051386- D00085
P01/7700 1.00-0222393.1

LONDON Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference

RJG/JLB/4087-GB

2. Patent number

0222393.1

26 SEP 2002

3. Full name, address and postcode of the or of each applicant (underline all surnames)

① University of Brighton
Mithras House
Lewes Road
Brighton BN2 4AT

② University of Sussex
Falmer
Brighton BN1 9QJ

Patents ADP number (if you know it)

① 7889413002

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

② 6254866003



4. Title of the invention

METHOD FOR SOIL REMEDIATION AND ENGINEERING

5. Name of your agent (if you have one)

Stevens Hewlett & Perkins

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Halton House
20/23 Holborn
London EC1N 2JD

Patents ADP number (if you know it)

1545003 ✓

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

Yes

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

See note (d)

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.
Do not count copies of the same document

Continuation sheets of this form

Description 9

Claim(s)

Abstract

Drawing(s)

1 + 1

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination
(Patents Form 10/77)

Any other documents
(please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

STEVENS HEWLETT & PERKINS

26.9.2002

12. Name and daytime telephone number of person to contact in the United Kingdom

Robert J Gaunt 020 7404 1955

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.

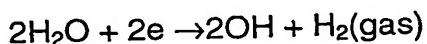
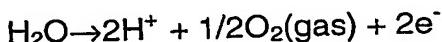
METHOD FOR SOIL REMEDIATION AND ENGINEERING

This invention relates to a method for electrokinetic soil remediation and engineering, and, more particularly, to such a method which involves the strategic electokinetic placing of an iron-rich barrier in soils, sediments and slurries.

Contaminated soils and groundwater at industrial, waste disposal and spill sites are serious environmental problems. Although clays and silts tend to sequester large quantities of heavy metals, radionuclides, and selected organic pollutants (e.g., Kovalick 1995), they are resistant to remediation with traditional technologies because of their low hydraulic conductivities. Electrokinetics is a process that separates and extracts heavy metals, radionuclides, and organic, inorganic, BTEX and radioactive wastes (e.g., Acar & Alshawabkeh 1993; Kovalick 1995; Virkutyte *et al.*, 2002).

The electrokinetic process involves a low intensity direct current (DC) applied across electrode pairs that have been implanted on the ground each side of the contaminated soil mass. When DC electric fields are applied to contaminated soil via electrodes placed into the ground, migration of charged ions occurs. Positive ions move towards the negatively charged cathode, while negative ions are attracted to the positively charged anode. It has been shown that non-ionic species are transported along with the electro-osmotically-induced water flow. Electrokinetic remediation is possible in both saturated and unsaturated soils.

The dominant and most important electron transfer reaction that occurs at the electrodes during the electrokinetic process is the electrolysis of water:-



The electric current causes electro-osmosis and ion migration, which moves the aqueous phase contaminants in the subsurface from one electrode to the other. Contaminants in the aqueous phase, or 5 desorbed from soil particles are transported towards respective electrodes depending on their charge. Commonly, contaminants are extracted by a secondary recovery system or deposited at the electrode. Recovery methods for contaminants that have migrated to the electrodes include electroplating, precipitation/co-precipitation, pumping near the electrode, or 10 complexing with ion exchange resins. Surfactants, complexing agents and reagents are frequently used to assist contaminant movement (e.g., Kovalick 1995; Virkutyte et al., 2002). However, most contaminated sites contain mixtures of wastes rather than single contaminants, which makes the decontamination process more complicated, and at present there is no 15 standardised universal soil/sediment remediation approach.

Electrodes that are inert to anodic dissolution are conventionally used in electrokinetic soil remediation. There include graphite, platinum, gold and silver electrodes, although less expensive electrodes made from titanium, stainless steel and plastic have also been 20 employed. Metals such as lead, chromium, cadmium, copper, uranium, mercury and zinc, as well as polychlorinated biphenyls, phenols, chlorophenols, toluene, trichloroethane and acetic acid are suitable for electokinetic remediation and recovery.

The main parameters that influence the overall process are 25 soil properties, depth and type of contamination, cost of accommodating electrodes and placing treatment zones, clean up time, and cost of labour (Virkutyte et al., 2002). Factors that influence the cost of the electrokinetic remediation process are soil characteristics and moisture, contaminant concentrations, concentration of non target ions and conductivity of pore 30 water, depth of the remediated soil, site preparation requirements, and electricity costs (van Cauwenbergh 1997). The cost optimised distance

between electrodes for commercial systems is 3 to 6m for most soils (Lagerman 1993; Ho et al., 1999). Given that the migration rate of contaminants is approximately 2 to 3cm/day, the time frame for successful remediation between electrodes spaced at 2 to 3m is of the order of 100 days, although cation-selective membranes are commonly employed to reduce remediation periods to 10 to 20 days (van Cauwenberghe 1997).

5 The breakdown of costs associated with a electrokinetic remediation programme are approximately 40% for electrode construction, 10 to 15% for electricity, 17% for labour, 17% for materials, and up to 16% for licenses and other fixed costs (Ho et al., 1997).

10

It is an object of the present invention to provide an improved method for electrokinetic soil remediation and engineering which is low cost, efficient and flexible in its application. This is achieved by the strategic electrokinetic placing of an iron rich barrier to a) remobilise and 15 trap contaminants in polluted soils, sediments and slurries; b) provide a physical barrier to waste spillages; and c) stabilise and strategically dewater/rewater soils.

According to the present invention there is provided a method for electrokinetic soil remediation and engineering which comprises applying a direct current across an area of soil, sediment or slurry so as to 20 generate a pH gradient and which promotes the *in situ* precipitation of a stable iron-rich band.

The method of this invention is characterised by increasing the mobility and solubility of contaminants through the application of an 25 electric charge and simultaneously arresting their migration by fixation to an electrochemically-generated ferric iron band which is precipitated within the area under treatment. This approach is distinct from other remediation techniques because it is geared towards deliberately producing an iron band *in situ* between the cathode and the anode, which simultaneously provides a physical as well as a chemical barrier; employs a low voltage of 30 typically less than 0.2 volts per cm distance between electrodes (with low

- energy requirements) to generate a strong pH gradient of typically from pH 2 to pH 13 within soils and sediments; uses low cost, sacrificial cathode and anode materials; can produce, through differential dewatering, controlled differential subsidence and permeability reduction; and which
- 5 can be generated in natural and industrial materials over laboratory timescales. In contrast, current commercial techniques have an order of magnitude higher energy requirements, actively avoid generation of a pH gradient and precipitation of iron or contaminants within the soil or sediment (e.g. current electrokinetic techniques); or use *ex situ* clean-up/disposal; or hard engineering technologies (e.g. permeable reactive barriers).
- 10

The present invention is a low voltage electro-chemical based technique, which uses electrokinetics to generate an intense pH gradient (pH 2 – pH 13) in soils, sediments and sludges, destabilise/dissolve minerals and force the *in situ* precipitation of a stable iron-rich band. Such iron-rich bands are found in natural rock and soil systems, where naturally occurring internal electric fields (with potential differences of the order of 1.0 to 1.5 volts) can produce bands of iron stone in unlithified sediments (e.g. Jacob *et al*, 1996). Such bands can result when the electrolytic dissociation of water takes place, with the formation of an anode zone characterised by acidic ions (pH 2.0 – 2.5), and a cathode zone characterised by alkaline ions (pH 10.5 – 11.5). As a consequence of the potential difference a sharp boundary zone is developed within which an abrupt pH change from 2.5 to 8 occurs. Where sufficient iron is present in the system, this is remobilised at the low pHs present in the anode zone, and spontaneously precipitated as insoluble metal hydroxides at the boundary zone of abrupt pH change (Jacob *et al*, 1996).

20

25

The method of the present invention thus emulates these natural iron^{III} mineralisation processes, but over laboratory rather than geological time scales, by applying a direct electric potential to electrodes to grow bands of iron^{III} mineral phases in sediment or soil columns, and to

30

harness their adsorptive properties, to trap pollutants from the aqueous phase, or desorbed from soil particles during their migration in the applied electrokinetic field. Freshly precipitated amorphous or poorly crystalline Fe and Mn-rich solids, of the type generated by this method, are extremely effective scavengers of a range of heavy metals, radionuclides and organic pollutants in a variety of environments (Bendell-Young and Harvey 1992, Cundy and Croudace 1995; N.B. iron is also known to dechlorinate toxic chlorinated hydrocarbons). Moreover, because this method generates strongly acidic conditions at the anode, contaminants attached to soil or sediment particles (such as radionuclides and heavy metals), which are soluble under acidic conditions are solubilised and forced to migrate towards the cathode, and subsequently (co)-precipitated with the iron-band. In essence, the present invention provides the opportunity to "flush" contaminants from contaminated sediments (e.g. plutonium), and then retrap them in the semi-permeable iron-band. This offers the potential of *in situ* clean-up of contaminated soils, sediments and sludges. Clean-up of the whole soil volume between the electrodes can be achieved, and plating of contaminants onto the cathode avoided, by simply reversing the polarity of the electrodes at regular intervals.

The approach embodied in the method of this invention is distinct from existing *in situ* remediation technologies, such as permeable reactive barriers, in that rather than merely sequestering contaminants from solution, the system actually mobilises contaminants into solution prior to their subsequent trapping by the reactive band, thus cleaning contaminated soils as well as ground waters. It differs from existing electrokinetic techniques in its use of low-cost electrodes, its low energy requirements and most significantly in its deliberate generation of a sorptive iron-band in the material being treated. Hence, the electrokinetic technique described here is innovative and clearly distinguished from other electrokinetic treatment systems. The precipitated iron band, however, represents much more than merely a chemical sink for toxic contaminants liberated from the

sediment column via oxidation-reduction and pH reactions. The electrokinetic process that triggers iron oxyhydroxide precipitation band formation may also be used to stabilise, and massively reduce the permeability of soils and sediments through differential dewatering of clays,

5 and iron-band generation. Hence, electrokinetic ferric iron precipitation represents a means of physically confining waste spills, providing a reactive barrier to liquid waste spillages that can be re-sealed and strengthened by periodic applications of electrical current (for instance in physically trapping and sorbing leachate that has percolated through the

10 base liner of a landfill). In addition, the method offers the potential, through strategic dewatering or rewatering of soils and sediments and iron-band generation, to rewater and stabilise soils for civil engineering applications (e.g. in building works). Existing dewatering techniques involve complete dewatering of large-volume slurries (e.g. Lamont-Black 2001) whereas the

15 present technique is applied *in situ* to strategically rewater or dewater parcels of soil, and so has a range of potential civil engineering applications (such as dealing with tree-induced subsidence in back gardens).

The method of this invention may have direct applicability in relation to the integrity of land fill liners, permeable reactive barrier

20 technologies, and funnel and gate systems, controlled differential subsidence, remediation of contaminated land (soils and sediments) and clean up of contaminated industrial sludges and slurries. Consequently, it will be of significant interest and potential benefit to a wide range of organisations, for example environment agencies, water companies, land

25 fill operators, civil engineering and environmental consultants and nuclear fuel companies.

The method of this invention will now be illustrated by the following example. Figure 1 referred to therein is a photograph which shows that by employing appropriate voltages an inert Fe(OH)^{III} bearing

30 band can be strategically grown, from point sources, through *in situ* precipitation in a sediment column, approximately equidistant between

electrodes.

Example

Pilot scale studies have been applied at laboratory scales in
5 25x2x15cm and 30x50x40cm open topped perspex cells (i.e. effectively in
two dimensional and three dimensional space). All experiments have been
run at <2 volts. Electrodes were fabricated from 25mm diameter cast iron
rods (Grade 250), composition: C 3.48%, Si 2.87%, Mn 0.812%,
S 0.099%, P 0.364%, Fe REM. The first experiments, working in a thirty
10 hour time frame with well sorted water saturated sands, resulted in the
generation of a continuous vertical iron band, part of which is depicted in
Figure 1. Initial permeability of the sands was 0.48×10^{-5} m/s, post
treatment permeability was recorded at 0.19×10^{-5} m/s. Experiments have
been run on a variety of contaminated muds, with groundwater and
15 seawater interstitial pore waters, under unsaturated and saturated
conditions. Time scales range from 3 to 400 hours. In every case a 1 to
4 cm thick, coherent, iron stone was generated *in situ*, approximately
equidistant between cathode and anode. For the mud experiments, initial
permeability was typically $\sim 0.29 \times 10^{-7}$, whereas treated material
20 permeability was recorded at 10^{-9} , or less, i.e. practically impervious. In
addition, clear dewatering was consistently observed in the sediment
around the anode, and rewatering around the cathode.

Chemical analyses have concentrated on copper bearing
mud from Southampton Water. Initial copper content was recorded by AAS
25 (Atomic Absorption Spectroscopy) at 88 parts per million (ppm). A set of
three spaced electrode pairs arranged 22cm apart were inserted. A
coherent, extractable, ironstone band with a thickness of up to 3cm was
generated from the point sources. The band occupied 14% of the cross
sectional area of the treated area. After 390 hours (16.3 days) of
30 electrokinetic treatment, the anode zone sediment showed a greater than
55% reduction in copper content (note that a proportion of the copper

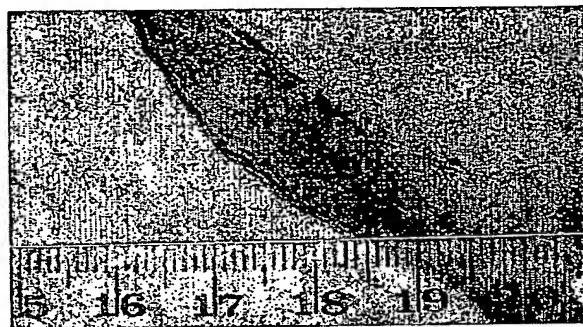
present is natural background copper, locked away in stable mineral interiors). Hydrocarbon-rich effluent was also forced to migrate out of the mud in the cathode zone under the applied electric field. The energy requirement for the experiment was 10.9 kW/m³, which compares
5 extremely favourably against commonly cited energy requirements for other electrokinetic remediation systems, e.g. 500kW h/m³ for removal of metal contaminants (e.g. Virkutyte *et al*, 2002). The time scale for copper decontamination of the sediment is comparable in duration to existing technologies which employ comparatively expensive cation-selective
10 membranes (van Cauwenberghe 1997). Moreover, given that the cast iron used as an electrode material in the method is comparatively inexpensive (compared to standard electrodes used in other techniques, e.g. gold coated electrodes and graphite), it appears that the experimental system is low cost in terms of energy, materials and electrode construction, which
15 typically make up ~70% of the costs associated with any electrokinetic remediation system (Ho *et al*, 1997).

REFERENCES

- 20 1. Acar Y.B, Alshawabkeh A.N (1993) Environmental Science and Technology **27**, (13) 2638-2647.
- 25 2. Bendell-Young L, Harvey H.H (1992) Geochim.Cosmochim.Acta **56**, 1175-1186.
3. Cundy A.B. and I.W. Croudace (1995) Journal of Environmental Radioactivity **29**, 191-211.
- 30 4. Ho S.V, Athmer C.H, Sheridan P.W, Shapiro A.P. (1997) Journal of Hazardous Material **55**, 39-60.

5. Ho S.V, Athmer C.H, Sheridan PW, Hughes BM, Orth R. McKenzie D, Brodsky P.H, Shapiro A.P, Thornton R, Salvo J, Schultz D, Landis R, Griffith R, Shoemaker S, (1999) Environmental Science and Technology, **33**, 1086-1091.
10. Hopkinsón L, Roberts S, Herrington R, Wilkinson J (1998) Geology **26**, 347-350.
15. Jacob K-H, Dietrich S, Krug H-J (1996) Self organised mineral fabrics. In: Kruhl J.H, Fractals and dynamic systems in geoscience. Springer Verlag, Berlin, 259-268.
20. Kovalick W.W. (1995) In situ remediation technology: electro-kinetics. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response Technology Innovation Office, Washington, EPA542-K-94-007.
25. Lageman R (1993) Environmental Science and Technology, **27** (13) 2648-2650.
30. Lamont-Black J (2000) Ground Engineering **34**, 22-23.
35. Van Cauwenbergh (1997) Electrokinetics: Technology overview report. Groundwater Remediation Technologies Analysis Centre, 1-17.
40. Virkutyte J, Sillanpaa M, Latostenmaa P (2002) The Science of the Total Environment **289**, 97-121.

Figure 1: Sub-vertical, 1cm thick Fe-rich band generated in water-saturated sands after 30 hours application of a 1.5V potential difference between cast iron electrodes.



PCT Application
GB0304181



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

BLACK BORDERS

IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

FADED TEXT OR DRAWING

BLURRED OR ILLEGIBLE TEXT OR DRAWING

SKEWED/SLANTED IMAGES

COLOR OR BLACK AND WHITE PHOTOGRAPHS

GRAY SCALE DOCUMENTS

LINES OR MARKS ON ORIGINAL DOCUMENT

REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.